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NASA
Headquarters
Washington 25, D.C.

ATTN: Mr. Roland H. Chase, Technical Director
        Code RET

Subject: MIROS Progress Letter No. 5, Sep. 20...
  NASA   Contract No. NASw-703

Dear Mr. Chase: W. E. Ward [1963] 13p ref

        This letter is a statement of progress made during the period covering
September 20 to October 20, 1963. This period included the last analytical
period prior to beginning the experimental program phase. Therefore it included
both preparatory experimental work and analysis.

Work Accomplished

        During this period as stated in the above paragraph, both theoretical
and preparatory experimental work was accomplished. Emphasis was placed on the
two modulation transfer schemes involving the mercury gas cell and the alkali-halide
color center crystals. As of this report the mercury gas cell experiment is
nearly set up; some final glass-work remains to be completed before the necessary
components, which have now arrived at Aerospace, can be put together. This
experiment can therefore be said to be ready to begin.

        The alkali halide color-center crystal experiment is lagging some-
what behind the mercury cell scheme because of two reasons: 1. experimental
preparations were started about a week after the mercury cell preparations, and
2. the necessity of creating our own F-center crystals here at Aerospace.

Analysis of the F-center modulation transfer scheme is now practically complete and the essential parts of it are included below.

Color Centers and Optical Modulation

In order to understand how passive optical mudulation transfer can be realized with color center crystals some introductory explanations will be helpful. Color centers are actually a result of crystal impurities, i.e. departures from regular crystal structures. In particular, the color centers of present interest result from the absence of a negative ion in the crystal lattice such as the absence of of the chlorine ion in an otherwise regular face centered cubic crystal of NaCl. This absence manifests itself as an apparent positive charge at the position normally occupied by the negative ion.

This positive "charge" may act as a nucleus about which an electron can orbit in a manner analogous to the hydrogen atom. Much theoretical work has appeared which is based on this simple picture and the results are in good agreement with experiment.

The color center, which gives rise to spectral absorption in selected bands giving the color center its name, arises from transitions in this electron-hole combination. However, spectral absorption involves less energy, and consequently lower frequencies than the hydrogen atom because the binding energies of the exciton are less than in the hydrogen atom.

When light of the proper wavelength is incident on a color center crystal the electron in the exciton will therefore absorb some of this radiation and be transferred to a higher orbit. In this excited state, the electron can either return to its ground state or absorb enough thermal energy to break entirely free from the positive hole. In the latter case, the electron has moved

into the crystal continuum, that is, into the conduction band of the crystal.
The proportionate number of ionizations of course depends on the temperature and
can be expressed by the formula $N = \frac{B}{A+B}$ where N is the number of completely
ionized electrons, A is the probability per unit time that an excited electron
will fall back to the ground state, and B is the probability per unit time that
the electron will be ionized <u>from the excited state</u>. A is of the order $5x10^7 sec^{-1}$
and experiments yield a value of B of the order $8.3x10^8 sec^{-1}$ therefore $N = \frac{8.3}{8.80} =$
.94. This calculation, carried out for NaCl, is generally true for the class of
crystals known as the alkali halides and indicates, that, at room temperature
an excited electron is much more likely to become ionized than to return to its
ground state. An extensive series of experiments by Pohl in Germany in the late
30's on the relation between photoionization and temperature substantiate this
conclusion.

If a plot is made of quantum efficiency in terms of photo current vs.
number of incident photons, the surprising result is obtained that the quantum
efficiency can be equal to two. A satisfactory explanation for this result is
that, once in the conduction band of the crystal, the most likely trapping center
for an electron is not the positive hole (negative ion vacancy) from which the
electron was ionized, but another color center. A rough calculation of the life-
time of a conduction electron in the presence of 10^{18} color centers per c.c. at
room temperature indicates it to be around 10^{-10} sec. As a result of this cap-
tive, the negative ion vacancy is now orbited by two electrons each of which is
bound less tightly to the "nucleus". Evidently, the sequence of photon absorp-
tion, ionization and subsequent captive results in the destruction of two color
centers, hence a maximum quantum efficiency of two.

AIR ARM DIVISION

Because of the smaller binding energies of these F-centers a new optical absorption band appears which is at longer wavelengths (red and infrared) than the origonal absorption ands. At the same time, the original absorption band has become bleached to some extent. These new color centers are relatively stable even at room temperatures. This is indicated by the fact that the average lifetime of these F-centers when kept in a dark room at room temperature is several hours. It should be added that this lifetime is not indicated by the optical binding energy but because of a peculiarity of ionic crystals the binding energy is determined by thermal processes, which in this case lead to a value for the binding energy of about half that of the binding energy as determined by quantum absorption.

This new color bond can be bleached just as the origonal color band is bleached when the new band is formed. In a permanently colored crystal, bleaching the F absorption band results in recreating the origonal color band. This process evidently can be continued indefinitely, a fact which suggests a possible modulation transfer scheme.

Production of Colored Crystals

It has been found that color centers in crystals can be produced in two ways; 1. By bombarding the crystal with high energy radiation such as X-rays, beta rays, gamma rays, etc., 2. By diffusing an alkali metal onto an alkali halide crystal. The first operation produces the necessary negative ion vacancy by physically displacing the negative ion. This results in no decrease in crystal density since negative ions do not leave the crystal, and also a gradual bleaching of the crystal as the ions slowly return to their proper sites. This operation therefore does not produce a permanently colored crystal. The second operation produces color centers when a negative ion leaves its location and jumps to

the crystal surface to form, with the adsorbed positive ion, a new crystal stratum, leaving a positive hole and a free electron. In this case there is a permanent excess of positive ions and consequently a permanently colored crystal. This crystal has less density than a normal crystal. Based on these considerations, it has been decided to create colored crystals by a diffusion method rather than by radio-active irradiation.

Characteristics of Colored Crystals

The range of absorption bands depends on the particular crystal. Lithium Chloride absorbs in the near ultra-violet; Sodium chloride absorbs near the yellow, potassium chloride near the red, and so on. There are many different crystals from which to choose as well as many combinations of crystals with themselves or with other materials. Evidently a broad class of possibilities is available.

The spectral width of these F centers follows a temperature dependence very nearly defined by the equation $h\Delta\nu = \sqrt{h\nu_0 kT}$, where $\Delta\nu$ is the spectral width of the band, h is Planck's constant, k is Boltzmann's constant, T is the absolute temperature, and ν_0 is the central frequency of the band. This width arises because of thermal lattice vibrations. Fig. I which is taken from Mott and Gurney, "Electronic processes in Ionic Crystals" shows the temperature dependence of the absorption band of potassium bromide.

As explained above, there is another temperature dependence which has an important bearing on the MIROS scheme. This involves the transistion from F to F' centers which can only occur if the excited F electron acquires sufficient thermal energy to move into the crystal conduction band. Therefore in any modulation scheme which makes use of F to F' transitions, account will have to be taken of this temperature dependence. A graphical indication of the temperature
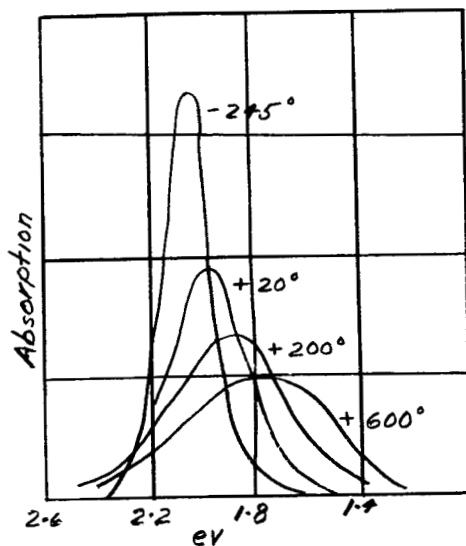
Figure 1

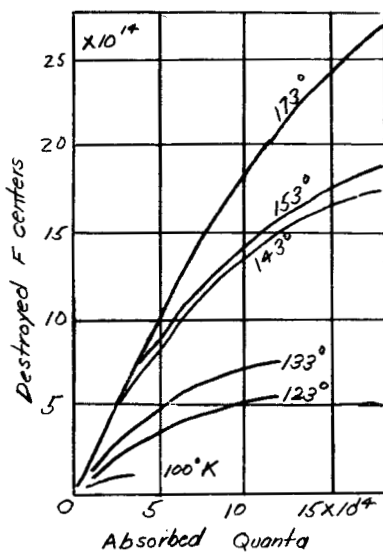Temperature Dependance of the F Absorbtion Band

Figure 2

Temperature Dependence of
F Center Destruction Efficiency

dependence in these colored crystals is given in Fig 2 taken from the work of Pohl. This curve is a plot of quantum yield of F' centers vs. temperature when irradiated with F light. The explanation for the low quantum yield at low temperatures is that the thermal energy acquired by the electron is too small to allow it to escape into the conduction band of the crystal, a necessary pre- quisite to producing an F' center. The temperature dependence of the stability of F' centers was also discussed above and has been inferred in a series of experiments by Pohl in which he measured the photo-ionization current as a function of frequency. He showed that at low temperatures $\sim -200°C$ no photo- current was measured upon irradiation with light in the F spectrum, due of course to insufficient thermal energy. At room temperature he obtained photo current immediately upon irradiation which ceased abruptly when the irradiation ceased. When he then irradiated the crystal with light in the F' spectrum, a photo current ensued which decayed in time. This was due to the absorption of photons in the F' band, which immediately upon absorption was followed by a transition of the F' electron into the conduction band. Obviously, if the temperature is high enough to ionize excited F electrons it will surely be high enough to ionize excited F' electrons. When the temperature was increased to about $235°C$, no additional current followed irradiation in the F' spectrum indicating that at this elevated temperature the F' centers are not stable.

These phenomena are characteristic of all the alkali halides. The numbers cited in this report have been taken at random from some particular alkali halides and will vary through the series of crystals even though the gen- eral dependences will hold for all of them. More data will be given in later reports.

Modulation Transfer With Color Center Crystals

In view of the phenomena discussed above, a possibility of using color centers in a modulation transfer scheme has presented itself in the form of F to F' center transitions. In order to investigate this scheme quantitatively it is necessary to consider the possibilities that might occur in F F' transitions, namely; 1. A photon absorbed in either the F or F' band region can lead to the production of an electron in the conduction band, and 2. Once an electron is in the conduction band it can be captured by a negative ion vacancy (forming an F center) or by an F center (forming an F' center). There are therefore four populations to consider: negative ion vacancies, F centers, F' centers, and the population of conduction band electrons. One attack on the problem begins by setting up the rate equations for these four levels:

$$\dot{n}_F = -I_F B_F n_F - P_F n_c n_F + P_o n_c n_o + I_{F'} B_{F'} n_{F'}$$

$$\dot{n}_{F'} = -I_{F'} B_{F'} n_{F'} + P_F n_c n_F$$

$$\dot{n}_o = +I_F B_F n_F - P_o n_c n_o$$

$$\dot{n}_c = I_F B_F n_F + I_{F'} B_{F'} n_{F'} - P_o n_c n_o - P_F n_c n_F$$

where

n_F is the density of F centers

$n_{F'}$ is the density of F' centers

n_o is the density of negative ion vacancies

n_c is the density of conduction electrons

I_F is the radiation density in the F region

B_F is the Einstein coefficient for F absorption

$I_{F'}$ is the radiation density in the F' region

$B_{F'}$ is the Einstein B coefficient for F' absorption

P_o is the probability per conduction electron per unit time for a negative ion vacancy to capture a conduction electron, and

P_F is the probability per conduction electron per unit time for a capture by an F center to form an F' center.

These equations are only approximate since they do not account for other trapping possibilities which are known to occur. However these other occurences are so rare that the approximation is good. Also, the assumption is implicit that an F or F' center is stable until a photon is absorbed, at which instant the electron moves into the conduction band. This is tantamount to the assumption that the crystal is operated at a temperature high enough to ionize excited F electrons, but not high enough to ionize unexcited F' electrons. This covers a broad temperature range.

From a solution of these rate equations, the time dependence of the two populations, F & F' can be determined, and consequently the corresponding absorption coefficients. Therefore a solution is obtained which yields the time dependence of the modulation. The solutions are tedious although not difficult.

The terms in the rate equations express mathematically the interesting if confusing processes that occur in F ⇌ F' conversion. The number of F centers can change in four ways; 1. By ionizing an F center (this creates a negative ion vacancy) 2. By capturing a conduction electron, (this creates an F' center) 3. By the capture of a conduction electron by a negative vacancy (this destroys a negative vacancy) 4. By ionizing an F' center (this destroys an F' center). Obviously the process is somewhat more complicated than transitions between atomic energy levels since destruction of a negative ion vacnacy or an F' center implies creation of an F center, while destruction of an F center implies either simultaneous creation of an F' center or of a negative ion vacancy. Even in

an extreme case in which no conduction electrons are captured either by F centers or negative ion vacancies, absorption of a photon in the F' region leads automatically to the creation of an F center. This fact is expressed by the rate equations when the capture probabilities, P_F and P_o are set equal to zero, in which case they take the form

$$n_F = - I_F B_F n_F + I_{F'} B_{F'} n_{F'}$$

$$n_{F'} = - I_{F'} B_{F'} n_{F'}$$

$$n_o = I_F B_F n_F$$

$$n_c = I_F B_F n_F + I_{F'} B_{F'} n_{F'}$$ from which a solution for $n_{F'}$ and n_F

is readily obtained;

$$n_{F'} = n_{F'}^o \, e^{- I_{F'} B_{F'} n_{F'} t}$$

$$n_F = \frac{n_{F'}^o}{I_F B_F - I_{F'} B_{F'}} \left\{ e^{- I_{F'} B_{F'} t} - e^{- I_F B_F t} \right\} + n_F^o \, e^{- I_F B_F t}$$

After sufficient time has elapsed, all the electrons will appear in the conduction band. The number of electrons in the conduction band will then equal the sum of the origonal number of F centers plus twice the origonal number of F' centers since each F' center contains two electrons. The number of negative ion vacancies will then equal the origonal number of F centers plus the origonal number of F' centers. At this time, if light in the F region is turned off while light in the F' is left on there will be a large increase in the number of F centers while the formation of F' centers is inhibited by F' radiation. Although this pololation distribution is unlikely the above discussion illiminates the problem as well as emphasizing the processes which occur in an alkali halides upon irradiation.

One possible modulation scheme is achieved by using radiation in the

F' region as the receiver which would presumably be continuously incident on the crystal while the transmitter radiation, falling in the F spectral region, is pulsed. These pulses should, according to the above considerations, create a momentary increased population of F' centers which is manifested in the receiver beam by an increased absorption. An estimate of the modulation induced by the transmitter can be obtained by assuming that momentarily all the absorbed photons lead to the creation of F' centers. Let the modulation be defined by the expression

$$M = \frac{e^{-k_{F'}N_{F'}\ell} - e^{-k_{F'}(N_{F'} + \Delta N_{F'})\ell}}{e^{-k_{F'}N_{F'}\ell}}$$

where

$N_{F'}$ - is the density of F' centers

ℓ - is the length of the crystal, and

$\Delta N_{F'}$ - is the change in the density of F' centers.

This equation can be solved for $\Delta N_{F'}$ in terms of M;

$$\Delta N_{F'} = \frac{1}{k_{F'}\ell} \ln \left\{ \frac{e^{+k_{F'}N_{F'}\ell}}{1 - M} \right\} - N_{F'}$$

Consider now, a photon density of E photons/cm^2-sec incident on the face of the crystal. In a short pulse of duration, τ, $\frac{\tau E \eta}{\ell}\left\{1 - e^{-k_F N_F \ell}\right\}$ photons will be absorbed per unit volume by the crystal, where

k_F is the absorption cross section per atom for the F band

N_F is the density of F centers

η is the F to F' conversion efficiency which will in general depend on time, on the incident power of both beams, on temperature and on crystal impurities.

When the two quanties are equated and an expression for power is obtained in terms of E, i.e. $Eh\nu = P$, the resulting expression gives a workable

estimate of the power in watts/cm^2 required to produce a given modulation:

$$P = \frac{h\nu_F \ell}{\eta\tau\left[1 - e^{-k_F N_F \ell}\right]} \left\{ \frac{1}{k_{F'}\ell} \ln\left(\frac{e^{+k_{F'} N_{F'} \ell}}{1 - M}\right) - N_{F'} \right\} \text{watts}/_{cm}2 .$$

This expression should prove quite useful in estimating such vague parameters as conversion efficiency in terms of the other values since each of its quantities is readily measured.

As a simple exercise consider the power required to produce a modulation, M, when the initial density of F' centers is zero, the quantum efficiency is unity and ℓ is one centimeter. k_F is known to be of the order of 2.6 x 10^{-16} cm^2. $k_{F'}$ can be estimated by noting that the F' band is about 2 1/2 times wider than the F band. If it can be assumed that the integrated absorption coefficients are equal, $k_{F'}$ should be 2 1/2 times smaller than k_F. Putting these quantities into the equation, and using $\lambda_F = {}^c/_{\nu_F} = 6000\text{Å}$

$$P = \frac{3.16 \times 10^{-3}}{\tau} \ell n \left[1 - M\right]^{-1} \text{watts}/_{cm}2$$

Some remarks should be made about the general expression for P, in particular about the quantities $N_{F'}$ and η. In the derivation of this expression there was the implicit assumption that during the period that the pulse is on there is no change in the density of F centers or the quantum efficiency while the density of F' centers increases. In other words, the F' light sees an increased absorption while the F light detects no change. This of course is unrealistic. For purposes of experimental results, this defect could be compensated by ascribing an exponential time dependence to the quantum efficiency, i.e. $\eta = \eta_0 e^{-\alpha t}$, where η_0 depends on the incident light in both F & F' bands, temperature, impurities etc., but not on time, while α characterizes the time

decay of the process. Therefore it seems that this expression should be quite helpful, generally, in discussing passive optical modulation transfer in these crystals.

Conclusion

The above discussion represents a partial sum of research and theoretical work preliminary to setting up the alkali halide experiment. It is not yet complete in either sense; new papers are appearing every day on the subject, to say nothing of the volume of literature left to peruse while the theoretical work will become more refined, in particular with respect to other processes than F - F' transitions which occur in alkali halides. These processes were neglected mainly for purposes of clarity but subsequent work will take account of them. It is hoped that this report will give a satisfactory indication of the present MIROS work with the alkali halides.

Plans for Next Period

During the next period it is expected that the mercury absorption cell experiment will be under way and that a report can be made of its first results. The experimental work with alkali halides is also starting and concentrated efforts are under way to complete the laboratory set up. As usual research and analysis will continue and future reports will contain the analyses similar to the present one.